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**(54) INK-JET RECORDING MATERIAL FOR NON-AQUEOUS INK****TINTENSTRAHLAUFEICHNUNGSMATERIAL FÜR NICHTWÄSSIGE TINTE****MATERIAU D'IMPRESSION A JET D'ENCRE POUR ENCRE NON AQUEUSE**

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## Description

## TECHNICAL FIELD

5 [0001] The present invention relates to an ink jet recording material used for recording by printers, plotters, and such which utilize an ink jet recording system using non-aqueous ink. More particularly, it relates to a so-called plain paper type ink jet recording material having no pigment-containing coating layer on the recording surface, especially an ink jet recording material for use with non-aqueous ink having excellent bleed resistance with no compromise in absorption of non-aqueous ink containing a high-boiling point petroleum solvent.

10 BACKGROUND ART

[0002] In the ink jet recording system, inks prepared by dissolving or dispersing a dye or pigment in an aqueous or oleaginous solvent have been used. Most popular among such inks are water-soluble dye inks made by dissolving various types of water-soluble dye in water. Water-soluble dye inks are advantageous for the maintenance of ink discharge head of ink jet recorder, and also excel in color development after printing and in resolution. This type of ink, however, has problem in water resistance of the recorded image as the ink is soluble in water. Also, since water-soluble dyes are normally poor in weather resistance (likely to cause discoloration or disappearance of the image by the effect of light, air, temperature or humidity), rapid discoloration or disappearance of the image may take place when the recorded medium is put on display outdoors.

[0003] Further, ink jet recording using aqueous ink poses various problems associated with stretch of the printed portion of the recording material which occurs as it absorbs the solvent (mostly water) in ink. Such stretch of the recording material takes place as the hydrogen bond between the fibers maintaining mechanical strength of the support is severed by the solvent, especially water, in the aqueous ink. This not only gives adverse effect to the conveyance of recording material in the printer but also reduces precision of the relative positional relation between recording material and printer head, giving rise to the various undesirable phenomena such as reduced dimensional precision of the drawings and non-uniformity of the image.

[0004] As a solution to these problems, JP-A-57-10660, JP-A-57-10661, JP-A-5-202324, JP-A-5-331397, etc., propose use of ink prepared by dissolving or dispersing a colorant in a non-aqueous solvent such as isoparaffinic hydrocarbons. According to these patents, it is possible to carry out ink jet recording with high dimensional precision and guaranteed against non-uniformity of image without causing any bit of stretch of the recording material. Further, because of low viscosity and low surface tension characteristic of non-aqueous solvents, it is possible to increase driving frequency of printer head as compared with ink jet recording using aqueous ink and to conduct recording at an amazingly high speed.

[0005] As for the recording material used for such ink jet recording using non-aqueous ink, JP-A-64-24785, etc., disclose a recording material having a coating layer comprising an oil-absorptive inorganic pigment, an organic pigment and an aqueous binder, while JP-A-1-255580, etc., describe a recording material comprising silica and an adhesive. These recording materials are the so-called matte coat type recording materials in which the recording surface has a matte-finished appearance.

[0006] On the other hand, in an effort for realizing recording material that can be used for both ink jet recording and electrophotographic recording, the so-called plain paper type ink jet/electrophotographic recording paper has been produced and placed on the market recently. In the hitherto proposed plain paper type ink jet recording paper, priority has been placed on realizing ink jet recording with aqueous ink, and little consideration has been given on adaptability to non-aqueous ink. Therefore, when recording is conducted on these recording materials with non-aqueous ink, there would occur seepage (or so-called bleeding) of the ink solvent which failed to be absorbed, or resolution would be reduced because of insufficient absorption of the ink solvent.

[0007] An object of the present invention is to provide a so-called plain paper type ink jet recording material for use with non-aqueous ink, which recording material has no pigment-containing coating layer on the recording surface, is used for recording by printers, plotters and such utilizing the ink jet recording system using non-aqueous ink, and has excellent bleed resistance with no compromise in absorbability of non-aqueous ink containing a high-boiling point petroleum solvent.

## DISCLOSURE OF THE INVENTION

55 [0008] The above object of the present invention can be achieved by means described in detail below.

[0009] In accordance with the present invention, in brief, there is provided an ink jet recording material on which recording is made with a non-aqueous ink having a non-aqueous solvent as main solvent, said recording material containing wood pulp and a filler which contains at least one substance selected from the group consisting of calcined

kaolin, precipitated calcium carbonate, aluminum hydroxide and magnesium hydroxide, the total content of said filler (s) being not less than 5% by weight and not more than 35% by weight measured as ash content according to JIS P8128, said recording material having improved bleed resistance with no compromise in non-aqueous ink absorbability.

5 [0010] Also, in case the boiling point of said non-aqueous solvent is 100°C or higher, there can be obtained a non-aqueous ink jet recording material having particularly high bleed resistance without impairing non-aqueous ink absorbability of the material.

[0011] Further, when the Bristow absorption coefficient of the non-aqueous solvent colored solution is made 50 ml/m<sup>2</sup>·sec<sup>1/2</sup> or greater, fixing quality of the non-aqueous ink is bettered, and an ink jet recording material for non-aqueous ink with very excellent ink absorbability can be obtained.

10 [0012] Still further, by making the density of the recording material not less than 0.60 g/cm<sup>3</sup> and not more than 1.05 g/cm<sup>3</sup>, non-aqueous ink fixing quality is even more bettered, providing a non-aqueous ink jet recording material with high-level ink absorbability.

#### MODE FOR CARRYING OUT THE INVENTION

15 [0013] The present invention is further illustrated by showing the preferred embodiments of the invention.

[0014] The present invention provides a plain paper type ink jet recording material containing wood pulp and a filler and suited for making recording with a non-aqueous ink. Said filler is at least one substance selected from the group consisting of calcined kaolin, precipitated calcium carbonate, aluminum hydroxide and magnesium hydroxide. Use of  
20 at least one filler selected from the group of said substances conduces to prevent the ink solvent from seeping out (bleeding) from the printed portion with the lapse of time without affecting ink absorbability of the material. It is yet to be accounted for why the presence of at least one filler selected from the group of calcined kaolin, precipitated calcium carbonate, aluminum hydroxide and magnesium hydroxide is effective for preventing bleeding, but it is considered that this phenomenon can be explained by the fact that these fillers have very strong affinity for the non-aqueous ink solvents  
25 and possess higher capability to adsorb and retain the bleeding solvent on the filler surface than the fillers used in the ordinary supports, such as talc, heavy calcium carbonate, etc.

[0015] Calcined kaolin usable in the present invention can be obtained in the various ways. Examples of such calcined kaolin include dehydroxylated, viz. partially calcined kaolin produced by calcining kaolinite at a temperature of approximately 650 to 700°C and perfectly calcined kaolin obtained from calcination at about 1,000  
30 to 1,050°C. calcined kaolin obtained by these methods maintains the hexagonal plate-like particle form same as before calcination, but it loses structural water to become amorphous and is increased in light scattering ability and adsorbing activity. Said calcined kaolin has the following general properties: TAPPI whiteness = 85 to 92; particle size = 60% or more is not greater than 2 µm; specific gravity = 2.4 to 2.7; specific surface area = 15 to 20 m<sup>2</sup>/g; oil absorption = 80 to 120 ml/100 g.

35 [0016] Precipitated calcium carbonate usable in the present invention is one obtained from synthesis by a chemical method unlike heavy calcium carbonate produced from physical crushing of natural limestone, and it is classified into crystal type, calcite type, aragonite type and vaterite type. Such precipitated calcium carbonate is widely used as filler or pigment in the paper-manufacturing industry. The methods available for producing said precipitated calcium carbonate include carbon dioxide combination method in which carbon dioxide is blown into milk of lime to react them,  
40 and carbonate solution combination method in which a carbonate is reacted with an aqueous solution of calcium chloride or such. At present, the former method (carbon dioxide combination method) is more popularly employed.

[0017] Generally, the primary particles of precipitated calcium carbonate have fusiform, needle-like, columnar, or locally rounded cubic or rectangular shape, and measure from about 0.05 to 1.0 µm in size. Usually, such fine primary particles of precipitated calcium carbonate form aggregates of several to a large number of particles, or so-called  
45 secondary particles.

[0018] Aluminum hydroxide usable in the present invention is a synthetic pigment made by extracting, for example, bauxite with sodium hydroxide to form sodium aluminate, and hydrolyzing it to precipitate the crystals. It is an inorganic pigment having a composition of Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O or Al(OH)<sub>3</sub>, and its monoclinic crystal form is hexagonal plate-like. It is commercially available, for example, under the trade name of Higilite from Showa Denko KK. It is stable in the pH  
50 range of 3.5 to 10.5.

[0019] Magnesium hydroxide usable in the present invention is produced, for instance, by reacting milk of lime with seawater to convert magnesium chloride in the seawater to magnesium hydroxide, which is precipitated.

55 [0020] The content of calcined kaolin, precipitated calcium carbonate, aluminum hydroxide or magnesium hydroxide in the recording material needs to be not less than 5% by weight and not more than 35% by weight as measured in terms of ash content defined in JIS P8128. When the content is less than 5% by weight, it is hardly possible to obtain the expected effect of the present invention, and when the content exceeds 35% by weight, paper layer strength of the recording material is excessively weakened to deteriorate printability of the recording material. These fillers may be used either singly or as a combination of two or more. In case of using two or more of the fillers in combination,

their amount added is adjusted so that the total content of the fillers will fall in the above-defined range of ash content. The "ash content defined in JIS P8128" means the ash content produced after heating at 900°C in case no calcium carbonate is contained, and after heating at 550°C in case calcium carbonate is contained.

5 [0021] If necessary, one or more of other types of filler, for example, mineral fillers such as talc, kaolin, clay, delamination kaolin, heavy calcium carbonate, magnesium carbonate, titanium dioxide, zinc oxide, magnesium sulfate, calcium silicate, aluminum silicate, magnesium silicate, calcium sulfate, silica, sericite, bentonite, smectites, etc., and organic synthetic fillers such as fine particles or hollow micro-particles of polystyrene resins, urea resins, acryl resins, melanine resins, benzoguanamine resins, etc., may be properly selected and added within limits not affecting the intended effect of the present invention. It is also possible to utilize fillers contained in wastepaper or broke by regenerating them. These other fillers may be added in any amount as far as the total content of calcined kaolin, precipitated calcium carbonate, aluminum hydroxide and magnesium hydroxide is not less than 5% by weight and not more than 35% by weight.

10 [0022] It is possible to further add other additives usually used in paper making, such as an internal additive sizing agent, paper strength reinforcing agent, etc., within limits not prejudicial to the effect of the present invention. The internal additive sizing agents usable here include neutral rosin-based sizing agents used for neutral paper making, alkenyl succinic anhydride, alkyl ketene dimers, petroleum resin-based sizing agents, and such. For the ink jet recording paper, however, it is preferable to use a neutral rosin sizing agent as a proof against strike-through since this agent exhibits a uniform sizing effect even at a small size.

15 [0023] As the paper strength reinforcing agent, the internal additives for paper making such as various types of anionic, nonionic, cationic or ampholytic paper strengthening agents are properly selected and used as required. For example, various kinds of starch, polyacrylamides, polyethylene-imine, polyamine, polyamide-polyamine, urea-formaldehyde resins, melamine-formaldehyde resins, plant gum, polyvinyl alcohol, latex, polyethylene oxide, polyamide resins and the like may be used either singly or as a proper combination of two or more.

20 [0024] Other internal additives for paper making such as coloring dye, coloring pigment, fluorescent brightener, pH adjuster, foaming agent, pitch controlling agent, slime controlling agent, etc., can be properly added in accordance with the purpose of use of the recording material.

25 [0025] For paper making according to the present invention, it is possible to use paper machines known in the paper-manufacturing industry, such as Fourdrinier paper machine, twine-wire paper machine, combination paper machine, cylinder paper machine, Yankee paper machine, etc. It is also possible to apply a resin, surface sizing agent and/or other additives in the course of paper making by such means as conventional size press, gate roll size press, film transfer size press or such.

30 [0026] The resins that can be applied by a size press in paper making according to the present invention include, for instance, oxidized starch, phosphoric esterified starch, home-made modified starch, cationized starch, other types of modified starch, polyethylene oxide, polyacrylamide, sodium polyacrylate, sodium alginate, hydroxymethyl cellulose, methyl cellulose, polyvinyl alcohol and their derivatives, which may be used either alone or jointly.

35 [0027] It is to be noted that the water-soluble cationic resins which are often used as a fixing agent or water repellent for aqueous ink may be unfavorable for ink jet recording material using non-aqueous ink because such resins are not only ineffective for fixing of ink but also rather act to promote infiltration of the ink solvent to encourage strike-through.

40 [0028] Surface sizing agent is optionally used for controlling infiltration of non-aqueous ink. Its main component is, for instance, styrene/acrylic acid copolymer, styrene/methacrylic acid copolymer, acrylonitrile/vinyl formal/acrylic ester copolymer, styrene/maleic acid copolymer, olefin/maleic acid copolymer, AKD, rosin or such.

45 [0029] "Bristow absorption factor" referred to in the present invention is the absorption factor  $K_a$  prescribed in JAPAN TAPPI paper pulp testing method No. 51 and the paper and paper board liquid absorption testing method (Bristow method). A non-aqueous solvent colored liquid was used as test liquid in the present invention. It is a non-aqueous colored liquid analogous to non-aqueous ink prepared from 80 parts of a high-boiling point solvent, 20 parts of oleyl alcohol and 0.1 part of a dye (Fat Red 7B). It is believed that there exists no simple interrelation between absorption factor of water and that of oil (non-aqueous liquid). When water infiltrates, the rate of infiltration tends to be affected by chemical disposition of the surface, causing a change in angle of contact. On the other hand, in the case of oil infiltration, as it is suggested that the angle of contact of oil with paper is 0°, it is possible to evaluate the porous structure of paper from absorption of oil. Details are given in "Short-time liquid infiltration measuring method - Bristow method" (Bulletin of Paper and Pulp Technology Association, Vol. 41, No. 8, pp. 33-45). The foregoing suggests that the absorption behavior of aqueous ink is totally different from that of non-aqueous ink, and it is quite unpredictable whether an ink jet recording medium suited for aqueous ink is also suited for non-aqueous ink as well.

50 [0030] In the present invention, the Bristow absorption coefficient determined by the above method is preferably 50 ml/m<sup>2</sup>·sec<sup>1/2</sup> or greater, more preferably 60 ml/m<sup>2</sup>·sec<sup>1/2</sup> or greater.

55 [0031] The density referred to in the present invention is the density of paper defined in JIS P8118, which is preferably not less than 0.60 g/cm<sup>3</sup> and not greater than 1.05 g/cm<sup>3</sup>. It is not clear why density is associated with non-aqueous ink absorbability, but as mentioned above in the explanation about the Bristow method, it is considered that non-

aqueous ink absorbability has relation to the porous structure of paper. This indicates that the density having interrelation with interfibrillar porosity is associated with absorbability. The higher the density, the less the interfibrillar porosity, hence the lower the non-aqueous ink absorbability. When density is too low, although voids are increased, retention (fixation) of the solvent (non-aqueous solvent) held there is weakened, making the solvent easier to effuse.

5 **[0032]** "Non-aqueous ink" referred to in the present invention designates ink for ink jet printers which contains as main components a non-aqueous solvent, a colorant (pigment and/or dye) and a dispersant. "Nonaqueous solvent" is a solvent having substantially no more than 5% by weight of water content, and it includes not only non-polar solvents but also polar organic solvents.

**[0033]** The non-aqueous solvent used in the present invention is selected from a variety of pertinent solvents in conformity to the characteristics of the ink discharge head of the ink jet recorder as well as the safety factors. In some cases, plural solvents may be used as an admixture. In the case of weak-scented petroleum solvents, since the components with different boiling points are mixed, the distillation temperature scatters and can not be represented by a specific boiling point. In the present invention, the solvent distillation temperature ranges from the initial boiling point temperature to the end point temperature, and the initial boiling point temperature is supposed to be the boiling point of the solvent. Regarding the boiling point of non-aqueous solvents, there are known the solvents having a boiling point of as low as around 60°C and those with a boiling point of as high as 300°C or even higher. In the present invention, the so-called high-boiling point solvents, or the solvents with a boiling point of 100°C or higher, especially 150°C or higher, are preferably used. If the boiling point of the non-aqueous solvent used is less than 100°C, undesirable phenomena such as gasification of the solvent tend to occur to cause drying of the ink or diffusion of such gasified solvent into the ambient air to generate offensive smell. Although the ink solvent essentially comprises such a high-boiling point solvent, there may be contained a small amount of a low-boiling point solvent for adjusting the viscosity and/or surface tension of the ink.

**[0034]** Exemplary of such solvents are petroleum naphtha solvents such as Pegasol (available from Mobil Petroleum Co., Ltd.), Shell SBR and Shellsol (both available from Shell Petrochemical Co., Ltd.), aromatic petroleum solvents such as Hisol (available from Nippon Sekiyu KK), aliphatic petroleum solvents such as Soltol (available from Phillips Petroleum Co., Ltd.), Exxsol, Isopar (both available from Exxon Chemical Co., Ltd.) and IP Solvent (available from Idemitsu Petrochemical Co., Ltd.), and naphthenic petroleum solvents such as Inksolvent (available from Mitsubishi Sekiyu KK). Examples of the polar organic solvents include alcohol, especially long-chain alcohol, glycol, polyglycol, their esters and ethers, especially mono- and di-alkylethers of glycol and polyglycol, and ketone. Esters of dicarboxylic acids, such as dioctyl sebacate, are also usable.

**[0035]** The colorants usable for non-aqueous ink include solutions or dispersions of oil-soluble dyes such as naphthol dye, azo dye, metal complex dye, anthraquinone dye, quinoimine dye, indigo dye, cyanine dye, quinoline dye, nitro dye, nitroso dye, benzoquinone dye, carbonium dye, naphthoquinone dye, naphthalimide dye, phthalocyanine dye, and perinine dye; carbon blacks such as furnace black, lamp black, acetylene black and channel black; organic pigments such as Ortho-nitroaniline black; Toluidine Red, Permanent Carmine FB, Fast Yellow AAA, Dis-azo Orange PMP, Lake Red C, Brilliant Carmine 6B, Phthalocyanine Blue, Quinacridone Red, Dioxane Violet, Victoria Blue, Alkali Blue Toner, Fast Yellow 10G, Ortho-nitroaniline Orange, Toluidine Red, Barium Red 2B, Calcium Red 2B, Pigment Scarlet 3B Lake, Anthocine 3B Lake, Rhodamine 6G Lake, Methyl Violet Lake, Basic Blue 5B Lake, Fast Sky Blue, Alkali Blue R Toner, Prussian blue, ultramarine, Reflex Blue 2G, Brilliant Green Lake, Phthalocyanine Green G, iron oxide powder, zinc white, calcium carbonate, clay, barium sulfate, alumina white, aluminum powder, daylight fluorescent pigment, and pearl pigment. Processed pigments obtained by conducting surface treatment on the above pigments are also usable. The colorants usable in the present invention are not limited to those mentioned above.

**[0036]** In the non-aqueous ink may be contained polar resins such as polyacrylates, linseed oil-modified alkyd resins, polystyrenes, rosin-based resins, terpenephenolic resins and alkylphenol-modified xylene resins for the purpose of improving shelf life or abrasion resistance after printing, and other additives such as metal blocking agent, surface tension modifier, surfactants, viscosity modifier, anti-foaming agent, defoaming agent, releasing agent, foaming agent, penetrating agent, fluorescent brightener, ultraviolet absorber, antiseptic, water resistance providing agent, rheology modifier and antioxidant in proper combinations.

**[0037]** The present invention will be explained in further detail with reference to the examples thereof, but it is to be understood that the substance of the present invention is not limited to these examples.

#### Example 1

55 **[0038]** 95 parts of LBKP (freeness: 450 mlcsf), 5 parts of NBKP (freeness: 500 mlcsf), 7 parts of calcined kaolin (trade name: Ansilex produced by Engelhard Co., Ltd.), 1.0 part of aluminum sulfate, 1.0 part of ampholytic starch (trade name: Cato 3210 produced by Nippon NSC Co., Ltd.), 0.3 part of neutral rosin sizing agent (trade name: NeuSize M-10 produced by Harima Kasei KK) and 0.02 part of an yield improver (trade name: NR-11LS produced by Hymo Corp.) were blended to prepare a 0.3% slurry. This slurry was processed into paper by a Fourdrinier paper machine,

treated by a sizing press to deposit oxidized starch (trade name: MS-3800 produced by Nippon Shokuhin Kakou KK) to a build-up of 1.2 g/m<sup>2</sup> in dry weight, and then subjected to 3-nip machine calendering to make recording paper of Example 1.

5 Example 2

[0039] The same procedure as specified in Example 1 was carried out except that calcined kaolin was blended in an amount of 12 parts to make recording paper of Example 2.

10 Example 3

[0040] The same procedure as specified in Example 1 was carried out except that calcined kaolin was blended in an amount of 20 parts to make recording paper of Example 3.

15 Example 4

[0041] The same procedure as specified in Example 1 was carried out except that calcined kaolin was blended in an amount of 30 parts to make recording paper of Example 4.

20 Example 5

[0042] The same procedure as specified in Example 1 was carried out except that calcined kaolin was blended in an amount of 40 parts to make recording paper of Example 5. The ash content of this recording paper was 31.4%, and its density was 0.78 g/cm<sup>3</sup>.

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Example 6

[0043] The procedure of Example 2 was followed except for skipping of 3-nip machine calendering to make recording paper of Example 6.

30

Example 7

[0044] The recording paper of Example 6 was supercalendered to make recording paper of Example 7.

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Example 8

[0045] The recording paper of Example 5 was supercalendered to make recording paper of Example 8.

Example 9

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[0046] The recording paper of Example 2 was supercalendered to make recording paper of Example 9.

Comparative Example 1

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[0047] The same procedure as specified in Example 1 was carried out except that calcined kaolin was blended in an amount of 4 parts to make recording paper of Comparative Example 1.

Comparative Example 2

50

[0048] The recording paper of Comparative Example 1 was supercalendered to make recording paper of Comparative Example 2.

Example 10

55

[0049] The same procedure as specified in Example 1 was carried out except that precipitated calcium carbonate (trade name: Tama Pearl TP121 produced by Okutama Kogyo KK) was used in place of calcined kaolin to make recording paper of Example 10.

Example 11

[0050] The procedure of Example 10 was followed except that precipitated calcium carbonate was blended in an amount of 12 parts to make recording paper of Example 11.

Example 12

[0051] The procedure of Example 10 was repeated except that precipitated calcium carbonate was blended in an amount of 20 parts to make recording paper of Example 12.

Example 13

[0052] The procedure of Example 10 was carried out except that precipitated calcium carbonate was blended in an amount of 30 parts to make recording paper of Example 13.

Example 14

[0053] The procedure of Example 10 was carried out except that precipitated calcium carbonate was blended in an amount of 40 parts to make recording paper of Example 14.

Example 15

[0054] The procedure of Example 11 was followed except for skipping of 3-nip machine calendering to make recording paper of Example 15.

Example 16

[0055] The recording paper of Example 15 was supercalendered to make recording paper of Example 16.

Example 17

[0056] The recording paper of Example 14 was supercalendered to make recording paper of Example 17.

Example 18

[0057] The recording paper of Example 11 was supercalendered to make recording paper of Example 18.

Comparative Example 3

[0058] The procedure of Example 10 was carried out except that precipitated calcium carbonate was blended in an amount of 4 parts to make recording paper of Comparative Example 3.

Comparative Example 4

[0059] The recording paper of Comparative Example 3 was supercalendered to make recording paper of Comparative Example 4.

Example 19

[0060] The same procedure as specified in Example 1 was carried out except that aluminum hydroxide (trade name: Higilite H-42 produced by Showa Denko KK) was used in place of calcined kaolin to make recording paper of Example 19.

Example 20

[0061] The procedure of Example 19 was followed except that aluminum hydroxide was blended in an amount of 12 parts to make recording paper of Example 20.

Example 21

[0062] The procedure of Example 19 was followed except that aluminum hydroxide was blended in an amount of 20 parts to make recording paper of Example 21.

Example 22

[0063] The procedure of Example 19 was followed except that aluminum hydroxide was blended in an amount of 30 parts to make recording paper of Example 22.

Example 23

[0064] The procedure of Example 19 was followed except that aluminum hydroxide was blended in an amount of 37 parts to make recording paper of Example 23.

Example 24

[0065] The procedure of Example 20 was followed except for skipping of 3-nip machine calendering to make recording paper of Example 25

Example 25

[0066] The recording paper of Example 24 was supercalendered to make recording paper of Example 25.

Example 26

[0067] The recording paper of Example 23 was supercalendered to make recording paper of Example 26.

Example 27

[0068] The recording paper of Example 20 was supercalendered to make recording paper of Example 27.

Comparative Example 5

[0069] The procedure of Example 19 was followed except that aluminum hydroxide was blended in an amount of 4 parts to make recording paper of Comparative Example 5.

Comparative Example 6

[0070] The recording paper of Comparative Example 5 was supercalendered to make recording paper of Comparative Example 6.

Example 28

[0071] The same procedure as specified in Example 1 was carried out except that magnesium hydroxide (trade name: KISUMA 5A produced by Kyowa Chemical Industries Co., Ltd.) was used in place of calcined kaolin to make recording paper of Example 28.

Example 29

[0072] The procedure of Example 28 was followed except that magnesium hydroxide was blended in an amount of 12 parts to make recording paper of Example 29.

Example 30

[0073] The procedure of Example 28 was followed except that magnesium hydroxide was blended in an amount of 20 parts to make recording paper of Example 30.



## Example 31

[0074] The procedure of Example 28 was followed except that magnesium hydroxide was blended in an amount of 30 parts to make recording paper of Example 31.

## Example 32

[0075] The procedure of Example 28 was followed except that magnesium hydroxide was blended in an amount of 37 parts to make recording paper of Example 32.

## Example 33

[0076] The procedure of Example 29 was followed except for skipping of 3-nip machine calendering to make recording paper of Example 33.

## Example 34

[0077] The recording paper of Example 33 was supercalendered to make recording paper of Example 34.

## Example 35

[0078] The recording paper of Example 32 was supercalendered to make recording paper of Example 35.

## Example 36

[0079] The recording paper of Example 29 was supercalendered to make recording paper of Example 36.

## Comparative Example 7

[0080] The procedure of Example 28 was followed except that magnesium hydroxide was blended in an amount of 4 parts to make recording paper of Comparative Example 7.

## Comparative Example 8

[0081] The recording paper of Comparative Example 7 was supercalendered to make recording paper of Comparative Example 8.

## Example 37

[0082] 95 parts of LBKP (freeness: 450 mlcsf), 5 parts of NBKP (freeness: 500 mlcsf), 4 parts of calcined kaolin (trade name: Ansilex produced by Engelhard Co., Ltd.), 3 parts of precipitated calcium carbonate (trade name: Tama Pearl TP121 produced by Okutama Kogyo KK), 1.0 part of aluminum sulfate, 1.0 part of ampholytic starch (trade name: Cato3210 produced by Nippon NSC Co., Ltd.), 0.3 part of neutral rosin sizing agent (trade name: NeuSize M-10 produced by Harima Kasei KK) and 0.02 part of a yield improver (trade name: NR-11LS produced by Hymo Corp.) were blended to prepare a 0.3% slurry. This slurry was processed into paper by a wire paper machine, treated by a size press to deposit oxidized starch (trade name: MS-3800 produced by Nippon Shokuhin Kakou KK) to a build-up of 1.2 g/m<sup>2</sup> in dry weight, and then subjected to 3-nip machine calendering to make recording paper of Example 37.

## Example 38

[0083] The same procedure as specified in Example 37 was carried out except that 3 parts of aluminum hydroxide (trade name: Higilite H-42 produced by Showa Denko KK) was used in place of precipitated calcium carbonate to make recording paper of Example 38.

## Example 39

[0084] The same procedure as specified in Example 37 was carried out except that 4 parts of aluminum hydroxide (trade name: Higilite H-42 produced by Showa Denko KK) was used in place of calcined kaolin to make recording

paper of Example 39.

#### Example 40

- 5 [0085] The same procedure as specified in Example 37 was carried out except that 4 parts of magnesium hydroxide (trade name: KISUMA 5A produced by Kyowa Chemical Industries Co., Ltd.) was used in place of calcined kaolin to make recording paper of Example 40.

#### Example 41

- 10 [0086] The same procedure as specified in Example 37 was carried out except that 3 parts of magnesium hydroxide (trade name: KISUMA 5A produced by Kyowa Chemical Industries Co., Ltd.) was used in place of calcined kaolin, and that 4 parts of aluminum hydroxide (trade name: Higilite H-42 produced by Showa Denko KK) was used in place of precipitated calcium carbonate to make recording paper of Example 41.

#### Example 42

- 15 [0087] The same procedure as specified in Example 37 was carried out except that 3 parts of magnesium hydroxide (trade name: KISUMA 5A produced by Kyowa Chemical Industries Co., Ltd.) was used in place of precipitated calcium carbonate to make recording paper of Example 42.

#### Comparative Example 9

- 25 [0088] The same procedure as specified in Example 37 was carried out except that 4 parts of heavy calcium carbonate was used in place of calcined kaolin to make recording paper of Comparative Example 9.

#### Comparative Example 10

- 30 [0089] The same procedure as specified in Example 37 was carried out except that 4 parts of talc was used in place of calcined kaolin to make recording paper of Comparative Example 10.

#### Comparative Example 11

- 35 [0090] The procedure of Example 2 was followed except that 12 parts of calcined kaolin was replaced by 12 parts of heavy calcium carbonate to make recording paper of Comparative Example 11.

#### Comparative Example 12

- 40 [0091] The procedure of Example 2 was followed except that 12 parts of calcined kaolin was replaced by 20 parts of talc to make recording paper of Comparative Example 12.

- [0092] Printing of a square solid printing pattern was conducted on the above recording papers of Examples 1 to 42 and Comparative Examples 1 to 10 with a non-aqueous black ink of the following formulation by an ink jet printer (PJ 3600 mfd. by Olympus Optical Industries Co., Ltd.), and evaluated in the following ways. Results are shown in Tables 1 to 3.

45 <Ink formulation>

#### [0093]

|    |  |          |
|----|--|----------|
| 50 | High-boiling point mixed solvent (Exxsol D110, initial boiling temperature: 243°C) | 60 parts |
|    | Oleyl alcohol  | 15 parts |
|    | Tripropylene glycol monomethyl ether   | 10 parts |
|    | Carbon black   | 11 parts |
| 55 | Polyesteramine-based dispersant  | 4 parts  |

## (1) Ink absorbability

5 [0094] "Ink absorbability" was evaluated by conducting single-color, two-color and three-color printing by an ink jet printer (PJ 3600 mfd. by Olympus Optical Industries Co., Ltd.) and visually observing the dried state of ink of the solid printed portions immediately after printing, giving the following rating: [5]: Printing could be done with no run-over of ink even in three-color printing; [4]: Printing could be done with no run-over of ink in two-color printing, but ink ran over slightly in three-color printing; [3]: There occurred slight run-over of ink and non-uniformity of printing although this posed no practical problem; [1]: Ink ran over heavily.

## 10 (2) Bleeding

[0095] "Bleeding" was evaluated by visually observing the seepage of ink solvent from around the three-color solid printed portions 24 hours after printing, giving the following rating: ○ : No seepage occurred; Δ : Slight seepage occurred, but it presented no practical problem; × : Seepage occurred conspicuously.

15 [0096] To provide referential data, similar evaluations were conducted with black ink (aqueous ink) using an Epson's ink jet printer PM770C.

## (3) Bristow absorption coefficient

20 [0097] "Bristow absorption coefficient" was determined in the following way.

<Test solution>

25 [0098]

|  |          |
|--|----------|
| A high-boiling point mixed solvent (Exxsol D110, initial boiling temperature: 243°C) | 80 parts |
| Oleyl alcohol  | 20 parts |
| Oil Violet (Fat Red 7B)  | 0.1 part |

30

<Bristow tester conditions>

[0099]

35 Slit width: 0.5 mm; slit length: 15 mm  
Amount of test solution: 50 μl  
Speed: 0.5 mm/sec to 250 mm/sec

[0100] Under the above conditions, the absorption factor  $K_a$  prescribed in JAPAN TAPPI paper pulp testing method No. 51 and the paper and paperboard liquid absorbability testing method (Bristow method) was determined.

40 [0101] Bleeding of non-aqueous ink is supposed to be well suppressed when the absorption factor  $K_a$  is 50 ml/m<sup>2</sup>·sec<sup>1/2</sup> or greater.

45

50

55

Table 1

|            | Filler<br>content | Density | Bristow<br>absorption<br>coefficient | Ink<br>absorba-<br>bility | Non-<br>aqueous | Bleeding<br>Aqueous |
|------------|-------------------|---------|--------------------------------------|---------------------------|-----------------|---------------------|
| Example 1  | 6.2               | 0.72    | 62                                   | 5                         | 0               | 0                   |
| Example 2  | 10.6              | 0.73    | 71                                   | 5                         | 0               | 0                   |
| Example 3  | 16.4              | 0.74    | 90                                   | 5                         | 0               | 0                   |
| Example 4  | 23.8              | 0.76    | 113                                  | 5                         | 0               | 0                   |
| Example 5  | 31.4              | 0.78    | 126                                  | 5                         | 0               | 0                   |
| Example 6  | 10.6              | 0.63    | 86                                   | 5                         | 0               | 0                   |
| Example 7  | 10.6              | 0.83    | 66                                   | 5                         | 0               | 0                   |
| Example 8  | 31.4              | 1.12    | 108                                  | 4                         | 0               | 0                   |
| Example 9  | 10.6              | 1.08    | 64                                   | 4                         | 0               | 0                   |
| Example 10 | 6.2               | 0.72    | 59                                   | 5                         | 0               | 0                   |
| Example 11 | 10.6              | 0.73    | 68                                   | 5                         | 0               | 0                   |
| Example 12 | 16.4              | 0.74    | 89                                   | 5                         | 0               | 0                   |
| Example 13 | 23.8              | 0.76    | 109                                  | 5                         | 0               | 0                   |
| Example 14 | 29.5              | 0.78    | 118                                  | 5                         | 0               | 0                   |
| Example 15 | 10.6              | 0.63    | 85                                   | 5                         | 0               | 0                   |
| Example 16 | 10.6              | 0.83    | 63                                   | 5                         | 0               | 0                   |
| Example 17 | 29.5              | 1.12    | 107                                  | 4                         | 0               | 0                   |
| Example 18 | 10.6              | 1.08    | 58                                   | 4                         | 0               | 0                   |

Table 2

|            | Filler<br>content | Density | Bristow<br>absorption<br>coefficient | Ink<br>absorba-<br>bility | Non-<br>aqueous | Bleeding<br>Aqueous |
|------------|-------------------|---------|--------------------------------------|---------------------------|-----------------|---------------------|
| Example 19 | 6.0               | 0.70    | 57                                   | 5                         | 0               | 0                   |
| Example 20 | 10.2              | 0.71    | 72                                   | 5                         | 0               | 0                   |
| Example 21 | 16.5              | 0.73    | 93                                   | 5                         | 0               | 0                   |
| Example 22 | 23.6              | 0.75    | 120                                  | 5                         | 0               | 0                   |
| Example 23 | 29.1              | 0.76    | 130                                  | 5                         | 0               | 0                   |
| Example 24 | 10.2              | 0.62    | 88                                   | 5                         | 0               | 0                   |
| Example 25 | 10.2              | 0.82    | 64                                   | 5                         | 0               | 0                   |
| Example 26 | 29.1              | 1.09    | 102                                  | 4                         | 0               | 0                   |
| Example 27 | 10.2              | 1.08    | 56                                   | 4                         | 0               | 0                   |
| Example 28 | 6.4               | 0.73    | 65                                   | 5                         | 0               | 0                   |
| Example 29 | 10.8              | 0.75    | 72                                   | 5                         | 0               | 0                   |
| Example 30 | 16.7              | 0.75    | 88                                   | 5                         | 0               | 0                   |
| Example 31 | 23.9              | 0.77    | 115                                  | 5                         | 0               | 0                   |
| Example 32 | 29.2              | 0.78    | 129                                  | 5                         | 0               | 0                   |
| Example 33 | 10.8              | 0.63    | 88                                   | 5                         | 0               | 0                   |
| Example 34 | 10.8              | 0.85    | 63                                   | 5                         | 0               | 0                   |
| Example 35 | 29.2              | 1.15    | 103                                  | 4                         | 0               | 0                   |
| Example 36 | 10.8              | 1.08    | 66                                   | 4                         | 0               | 0                   |

Table 3

|                    | Filler<br>content | Density | Bristow<br>absorption<br>coefficient | Ink<br>absorba-<br>bility | Non-<br>aqueous | Bleeding<br>Aqueous |
|--------------------|-------------------|---------|--------------------------------------|---------------------------|-----------------|---------------------|
| Example 37         | 6.2               | 0.72    | 60                                   | 5                         | 0               | 0                   |
| Example 38         | 5.6               | 0.71    | 61                                   | 5                         | 0               | 0                   |
| Example 39         | 6.4               | 0.70    | 63                                   | 5                         | 0               | 0                   |
| Example 40         | 6.0               | 0.72    | 62                                   | 5                         | 0               | 0                   |
| Example 41         | 5.9               | 0.71    | 64                                   | 5                         | 0               | 0                   |
| Example 42         | 5.4               | 0.71    | 65                                   | 5                         | 0               | 0                   |
| Comp.<br>Example 1 | 3.4               | 0.71    | 55                                   | 4                         | Δ               | 0                   |
| Comp.<br>Example 2 | 3.4               | 1.05    | 48                                   | 3                         | Δ               | 0                   |
| Comp.<br>Example 3 | 3.4               | 0.71    | 54                                   | 4                         | Δ               | 0                   |
| Comp.<br>Example 4 | 3.4               | 1.05    | 49                                   | 3                         | Δ               | 0                   |
| Comp.<br>Example 5 | 3.5               | 0.70    | 56                                   | 4                         | Δ               | 0                   |

Cont'd -

Table 3 (Cont'd)

|                     | Filler<br>content | Density | Bristow<br>absorption<br>coefficient | Ink<br>absorba-<br>bility | Non-<br>aqueous | Bleeding<br>Aqueous |
|---------------------|-------------------|---------|--------------------------------------|---------------------------|-----------------|---------------------|
| Comp.<br>Example 6  | 3.5               | 1.05    | 50                                   | 3                         | Δ               | ○                   |
| Comp.<br>Example 7  | 3.4               | 0.72    | 55                                   | 4                         | Δ               | ○                   |
| Comp.<br>Example 8  | 3.4               | 1.03    | 49                                   | 3                         | Δ               | ○                   |
| Comp.<br>Example 9  | 5.6               | 0.71    | 55                                   | 4                         | Δ               | ○                   |
| Comp.<br>Example 10 | 5.9               | 0.71    | 52                                   | 4                         | Δ               | ○                   |
| Comp.<br>Example 11 | 10.5              | 0.73    | 51                                   | 3                         | x               | ○                   |
| Comp.<br>Example 12 | 16.9              | 0.73    | 45                                   | 1                         | x               | ○                   |

[0102] As is seen from Tables 1 to 3, Examples 1 to 36, where the filler is at least one substance selected from the group consisting of calcined kaolin, precipitated calcium carbonate, aluminum hydroxide and magnesium hydroxide and the filler content is 5% by weight or higher, showed excellent bleed resistance when recording was conducted with non-aqueous ink. Also, Examples 1-7, 10-16, 19-25, and 28-34 where density is defined to the range of 0.60 to 1.05 g/cm<sup>3</sup>, showed particularly high ink absorbability. Comparative Example 11, where the filler is heavy calcium carbonate,

had poor bleed resistance in use with non-aqueous ink although no problem was raised in use of aqueous ink. Comparative Example 12 using talc as filler was bad in both ink absorbability and bleed resistance. Examples 37 to 42 using plural fillers excelled in both ink absorbability and bleed resistance when containing calcined kaolin, precipitated calcium carbonate, aluminum hydroxide and magnesium hydroxide as fillers. However, as shown in Comparative Examples 9 and 10, bleed resistance is poor when the amount of filler(s) of the present invention is less than 5% by weight, even if the total content of fillers is 5% by weight or higher.

#### INDUSTRIAL APPLICABILITY

[0103] According to the present invention, there is provided plain paper type recording paper which is proof against bleeding and shows excellent ink absorbability even when ink jet recording is conducted with non-aqueous ink.

#### Claims

1. An ink jet recording material for use with non-aqueous ink containing a non-aqueous solvent as main solvent, said recording material comprising wood pulp and a filler which comprises at least one substance selected from the group consisting of calcined kaolin, precipitated calcium carbonate, aluminum hydroxide and magnesium hydroxide, the total content of said filler being not less than 5% by weight and not more than 35% by weight as ash content prescribed in JIS P8128.
2. An ink jet recording material according to claim 1 wherein the boiling point of said non-aqueous solvent is 100°C or higher.

#### Patentansprüche

1. Tintenstrahl-Aufzeichnungsmaterial zur Verwendung mit einer nicht-wässrigen Tinte, enthaltend ein nichtwässriges Lösungsmittel als Hauptlösungsmittel, wobei das Aufzeichnungsmaterial Holzzellstoff und ein Füllmaterial umfasst, das mindestens eine Substanz umfasst, die ausgewählt wird aus der Gruppe bestehend aus calciniertem Kaolin, ausgefälltem Calciumcarbonat, Aluminiumhydroxid und Magnesiumhydroxid, wobei der Gesamtgehalt des Füllmaterials nicht weniger als 5 Gew.% und nicht mehr als 35 Gew.% als Aschegehalt gemäss JIS P8128 beträgt.
2. Tintenstrahl-Aufzeichnungsmaterial gemäss Anspruch 1, wobei der Siedepunkt des nicht-wässrigen Lösungsmittels 100°C oder mehr beträgt.

#### Revendications

1. Matériau d'impression à jet d'encre, à utiliser avec une encre non aqueuse contenant un solvant non aqueux en tant que solvant principal, ledit matériau d'impression comprenant de la pâte de bois et une charge qui comprend au moins une substance choisie dans le groupe formé de kaolin calciné, de carbonate de calcium précipité, d'hydroxyde d'aluminium et d'hydroxyde de magnésium, la teneur totale en ladite charge n'étant pas inférieure à 5% en poids, et pas supérieure à 35% en poids en tant que teneur en cendre, comme prescrit dans JIS P8128.
2. Matériau d'impression à jet d'encre selon la revendication 1, dans lequel le point d'ébullition dudit solvant non aqueux est de 100°C ou plus.



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